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Ultrasonic Processing of Aluminum Alloys for Grain Refining

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An overview on the ultrasonic processing of aluminum alloys during solidification is given. The fundamental issues on nucleation and growth mechanisms on the presence of cavitation are reviewed. Different mechanisms of ultrasound-assisted grain refinement, e.g. activation of inclusions, increased efficiency of grain refining particles and fragmentation, are discussed and illustrated with experimental data. It is demonstrated that the presence of potent nucleating particles is essential for obtaining considerable grain refining upon processing of molten alloys. The fragmentation and multiplication of nucleation sites is the main mechanism of structure refinement upon ultrasonic processing during solidification. Practical examples are given illustrating the technologically applicable schemes of processing. The formation of nondendritic structure in commercial aluminum alloys is the ultimate result of ultrasonic processing. The mechanism of nondendritic solidification is discussed. The implications of the nondendritic structure for the improvement of mechanical and technological properties are illustrated for foundry and wrought alloys. The challenges for the future research and application of ultrasonic solidification processing are outlined.

Keywords: *cavitation, ultrasonic processing, solidification, grain refinement, nondendritic structure, mechanical properties*

1. Mechanisms of grain refinement under cavitation

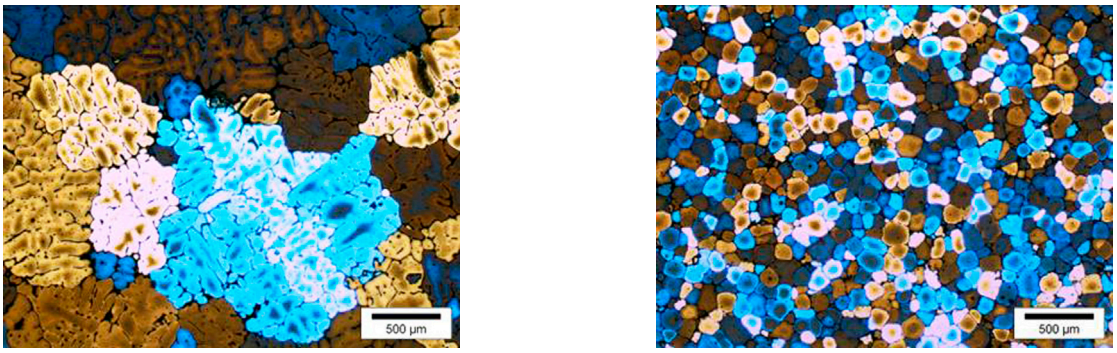
Ultrasonic treatment of molten and solidifying metals attracts attention of metallurgists, metals scientists, physicists and chemists for quite a long time. First reports on emulsification of dissimilar liquids and dispersion of solid particles in the liquid date back to the 1920s [1]. In the 1950s and 1960s a lot of laboratory and pilot scale trials have been performed mostly in Germany [2, 3] and Soviet Union [4, 5, 6] showing the possibility to apply cavitation phenomenon to structure refinement, improved mixing of immiscible metals, degassing and formation of metal-matrix ceramic-reinforced composites. First successful industrial-scale applications have been reported in the Soviet Union [5]. In the same period of time several hypothesis were suggested in an attempt to explain the observed phenomena.

The most popular mechanism is fragmentation of dendritic grains resulting in multiplication of grains. This mechanism works in most cases but does require the interaction of the cavitation zone with the solidification front. Figure 1 demonstrates the action of this mechanism. Therefore, the treatment should be performed below the liquidus, hence at rather low temperatures and the effect would be then limited to a relatively small volume. It is also not very technologically viable to perform the treatment inside the mold, whether it is the DC casting mold or the investment casting mold.

The other set of hypothesis deals with cavitation-induced heterogeneous nucleation.

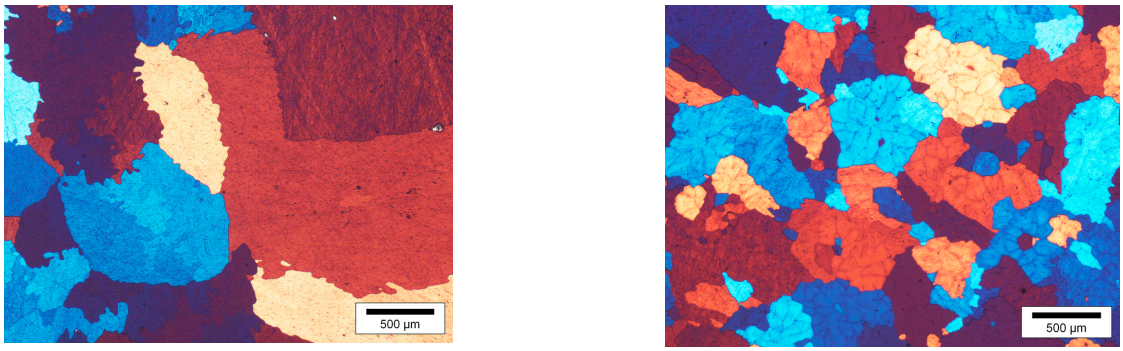
It was suggested [7] that the collapse of pulsating cavitation bubbles causes extremely powerful shock waves, The resultant sharp and local pressure increase leads to the reduction in solidification temperature, which in turn triggers nucleation in the cavitating melt volume (principle of Le Chatelier). Using the Clausius – Clapeyron equation, one can estimate that the local pressure can rise by 100 – 1000 MPa in the sonicated liquid with the melting point of aluminium increasing by several tens of degrees. An increase in the melting point is equivalent to increased undercooling, which will enhance nucleation. Another mechanism was proposed by Kapustina [4] and involves undercooling

of the bubble surface. During the expansion half-period, the bubble rapidly increases in size, and the liquid evaporates inside the bubble. The evaporation and expansion tend to reduce the bubble temperature. A decrease of the bubble temperature below the equilibrium temperature results in an undercooling of the melt at the bubble surface, and hence in the probability that a nucleus will be formed on the bubble. When such bubbles collapse they generate a significant number of nuclei, promoting heterogeneous nucleation in the melt.



a b

Figure 1. Effect of ultrasonic treatment in the solidification range of an Al–4% Cu alloy: (a) without UST and (b) with UST [8]



a b

Figure 2. Grain structure of a 99.97% aluminum after ultrasonic treatment: (a) without adding Al_2O_3 and (b) with Al_2O_3 additions [8]

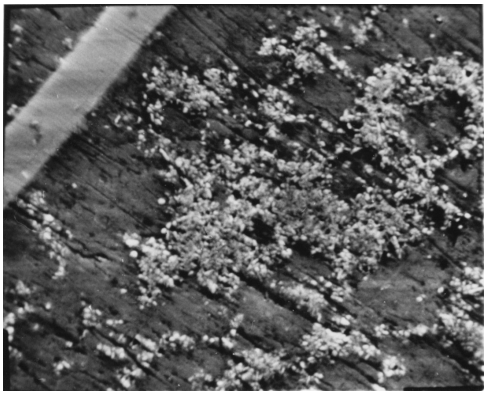
Yet another hypothesis has been suggested by G.I. Eskin [5, 9, 10]. Real melt always contains vast amount of very small nonmetallic particles that are purely wet by molten aluminum and usually remain inactive during solidification. In some cases high melt superheating may promote wetting of these particles with subsequent transformation of them in active solidification sites followed by grain refinement [11]. Ultrasonic (cavitation) treatment can do the same without melt superheating and on more microscopic scale, simultaneously preventing agglomeration of the particles. This mechanism acts as follows.

- Small particles , e.g. of alumina are stripped of molecular hydrogen absorbed on their surface;
- the liquid phase gets access to the surface;
- the surface tension decreases in the cavitation field so the melt can wet the particles;
- particles provide substrate for heterogeneous nucleation of intermetallic particles that act as substrates for aluminum;
- cavitation also decreases the capillary pressure allowing the liquid to penetrate in small defects on the particle surface;
- the equilibrium melting point in small capillaries is higher than in the bulk liquid and the melt solidifies there at temperatures above the alloy liquidus;

- solid aluminum alloy present in the surface defects of particles provide solidification site for nucleation and growth of aluminum.

This mechanism is more technologically attractive than the fragmentation as it allows one to treat the melt in essentially liquid (fluid) state, hence at higher temperatures and away from the solidification region. It is believed that the successful application of ultrasonic melt treatment upon DC casting (described later in this paper) involved this mechanism of grain refinement. To separate the activation of nonmetallic particles from other accompanying phenomena is not an easy task. Figure 2 demonstrates grain refinement of pure aluminum with additional of alumina particles.

The idea of treating the melt before the entry to the mold, e.g. in the melt transport system requires some creative thinking as the choice of grain refining elements, shorter treatment times, and the fading of the treatment effect should be taken into account. Two approaches can be suggested. The first takes advantage of the commercially applied technique of grain refining with a AlTiB master alloy rod introduced in the launder during DC casting. Such a master alloy contains TiB_2 particles that act as substrates for solid aluminum (possibly with the formation intermediate metastable Al_3Ti layer [12]). Only several percent of particles become active due to the size selection [13] and the rest of the particles either remain inactive or form agglomerates that become a serious problem, especially in high-strength and pure alloys. Ultrasonic treatment performed either in the location of AlTiB introduction or immediately after that may help in dispersing the agglomerates and activation of TiB_2 particles, combining the mechanisms of fragmentation and activation. The efficiency of this treatment is shown in Figure 3.



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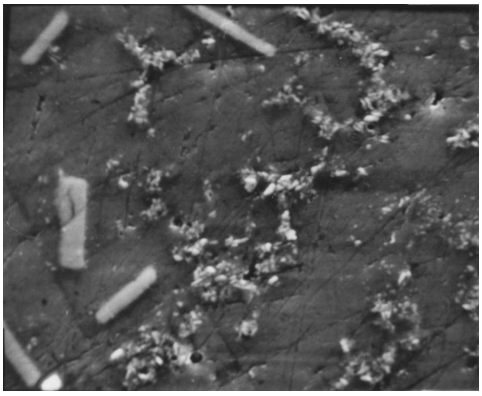

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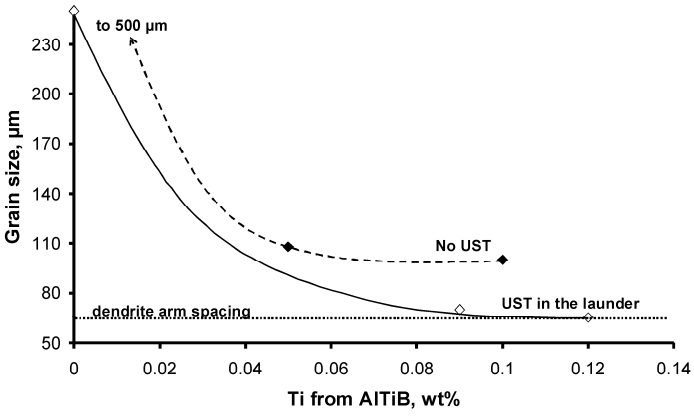


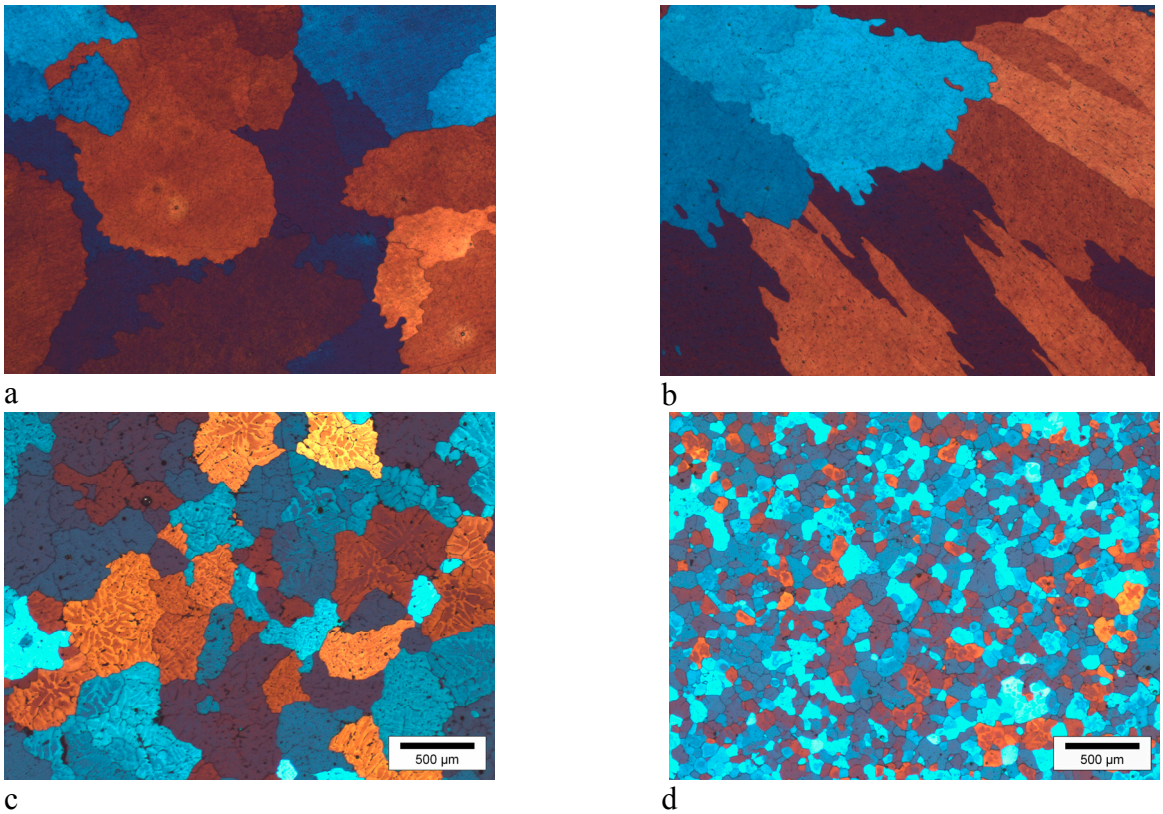
c

Figure 3. Effect of ultrasonic treatment on the structure of an AlTiB master alloy (a, without UST and b, with UST) and (c) the grain size in an Al–Cu–Mg–Mn alloy cast without and with UST treatment combined with AlTiB introduction in the launder [14]

The second approach deals with the intermetallic particles that are naturally present in the melt due to the alloy composition but may be affected by cavitation treatment and turned into very efficient solidification sites. It was long ago noted that the efficiency of ultrasonic melt treatment is improved when Zr is present in the alloy [5]. Zirconium forms primary intermetallic particles Al_3Zr which are

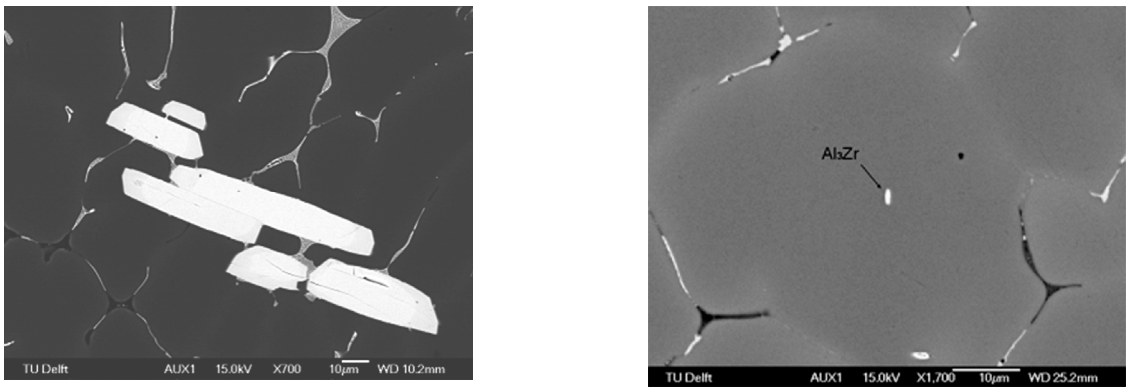
not very good grain refiner even after ultrasonic melt treatment as shown in Figure 4a, b. However, when small additions of Ti are present in the alloy the effect of ultrasonic treatment becomes very impressive (Figure 4c, d). In this case, cavitation results in refining of primary Al_3Zr particles (due to fragmentation) to the size when they become suitable for heterogeneous nucleation of aluminum (Figure 5), and at the same time Ti dissolved in Al_3Zr may change its surface properties for the benefit of aluminum nucleation. In this approach it is essential to perform treatment below the temperature of Al_3Zr formation but above the liquidus of the aluminum solid solution.

The grain refinement induced by ultrasonic (cavitation) treatment can be very efficient, up to the formation of so-called nondendritic grain structure, when aluminum grains do not have dendritic branches and at the same time are as small as the dendrite arm spacing typical of the given cooling rate. Some of the fundamental features of the nondendritic structure are described in the next section.



a b c d

Figure 4. Grain structures of an Al–0.2% Zr (a, b) and Al–0.2% Zr–0.06% Ti (c, d) alloys without UST (a, c) and with UST in the liquid state at 700 °C (b, d) [8]



a b

Figure 5. Particles of Al_3Zr in an Al–0.6%Zr–0.06% Ti alloy without (a) and with UST at 710 °C (b) [8]

2. Nondendritic structure: features and conditions of formation

It is well known that grains are formed from nucleation centers and grow in the undercooled liquid environment. Accumulation of rejected solute elements at the solid/liquid interface (constitutional undercooling) restricts growth and, at the same time, facilitates nucleation of new grains. The grain size is generally determined by the amount of active nucleation sites and the restriction of growth. The former is the function of undercooling (cooling rate), the latter – of chemical composition. The growth of grains under conditions of thermal and constitutional undercooling occurs in the dendritic manner, producing dendritic grains as shown in Figure 1a. It has been suggested, based on theoretical considerations and experiments on Mg–Zr alloys that if the amount of nucleation sites would be large enough to prevent the growth of grains then the grains will retain nondendritic shape (Figure 1b, 4d) and their size will be determined by the same factors as for dendrite arm spacing [15]. This idea was further developed and generalized by works performed in All-Russia Institute of Light Alloys (VILS) [9]. It was shown for a wide range of metallic alloys that the nondendritic structure represents the finest grain size achievable at the given cooling rate and indeed this grain size is equal to the secondary dendrite arm spacing of the dendritic grains in the same alloy cooled at the same cooling rate as shown in Figure 6. The only factor controlling the nondendritic grain size is the cooling rate.

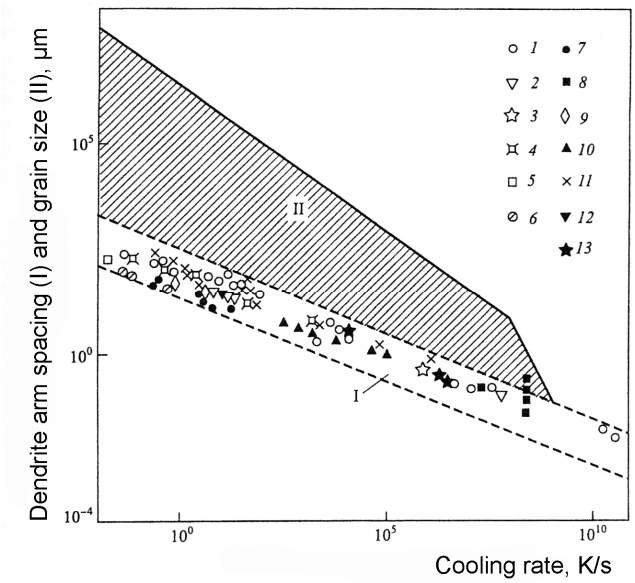


Figure 6. Effect of cooling rate in the size of nondendritic grain (1–3), dendrite arm spacing (4–13) for aluminum (1, 4–11), magnesium (2, 12) and nickel (3, 13) alloys

Nondendritic grains, though equal in size to the dendrite branches, differ significantly in crystallographic orientation being surrounded by large-angle boundaries (Figure 7a). The microsegregation pattern also shows more smooth and round isoconcentrates reflecting the growth regime of these grains (Figure 7b).

The necessary condition for the formation nondendritic structure during solidification is the formation of excessive amount of solidification sites for the grains, i.e. thermal and solute fields around each grain will overlap at the early stage of grain formation preventing their growth as dendrites. This can be achieved by different means, e.g. using very efficient grain refiners like Sc in Al alloys or Zr in Mg alloys, very high melt superheating followed by rapid solidification, or extremely high cooling rates. Cavitation melt treatment presents very attractive means of the formation of nondendritic structure, dealing with conventional alloys compositions and solidification conditions typical of commercial casting techniques.

The formation of nondendritic structure offers some advantages. First of all, the macrostructure of castings and billets is more uniform as compared to the castings and billets of the same size but with

dendritic grains structure. As a result the extent of macrosegregation and the susceptibility to hot and cold cracks are much less in the castings and billets with nondendritic structure. Indeed only the formation of nondendritic structure upon ultrasonic melt treatment allowed the commercial production of large, crack-free, round billets 960 to 1200 mm in diameter from high-strength aluminum 2XXX and 7XXX series alloys [9]. Secondly, the refinement of structure results in finer distribution of nonequilibrium eutectics. For example, nondendritic structure of a 7055-alloy billet features 65–80 μm grains with 0.3-μm eutectic layers whereas the same size billets with dendritic structure exhibit grains coarser than 1300 μm with the eutectic layer 3–6 μm thick. As a result, nondendritic structure allows for much shorter homogenization times as shown in Table 1. And thirdly, the mechanical properties of homogenizes billets are improved (Figure 8), which facilitates break-down and hot deformation of the billets and ingots.

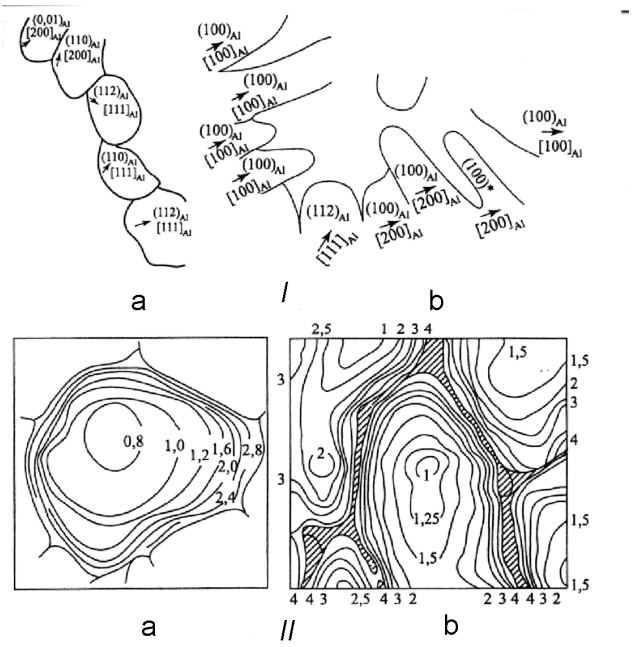


Figure 7. Crystallographic orientation (I) and microsegregation isoconcentrates (II) of nondendritic (a) and dendritic grains (b) in aluminum 7055 (I) and 2324 (II) alloys

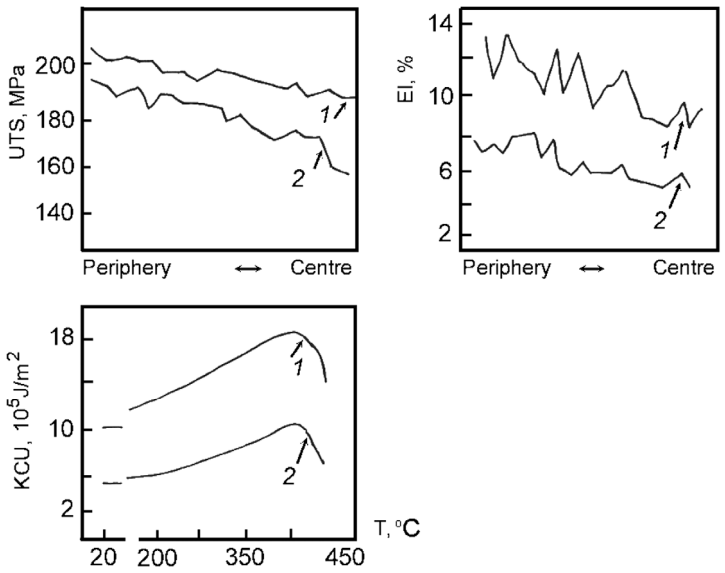


Figure 8. Distribution of room-temperature tensile properties in the cross-section of a 960-mm billet of a 7050 alloy and the impact toughness at different temperatures relevant to hot working: 1, nondendritic structure, DC casting with UST; 2, dendritic structure, DC casting without UST

3. Effect of nondendritic structure on structure and properties of deformed products

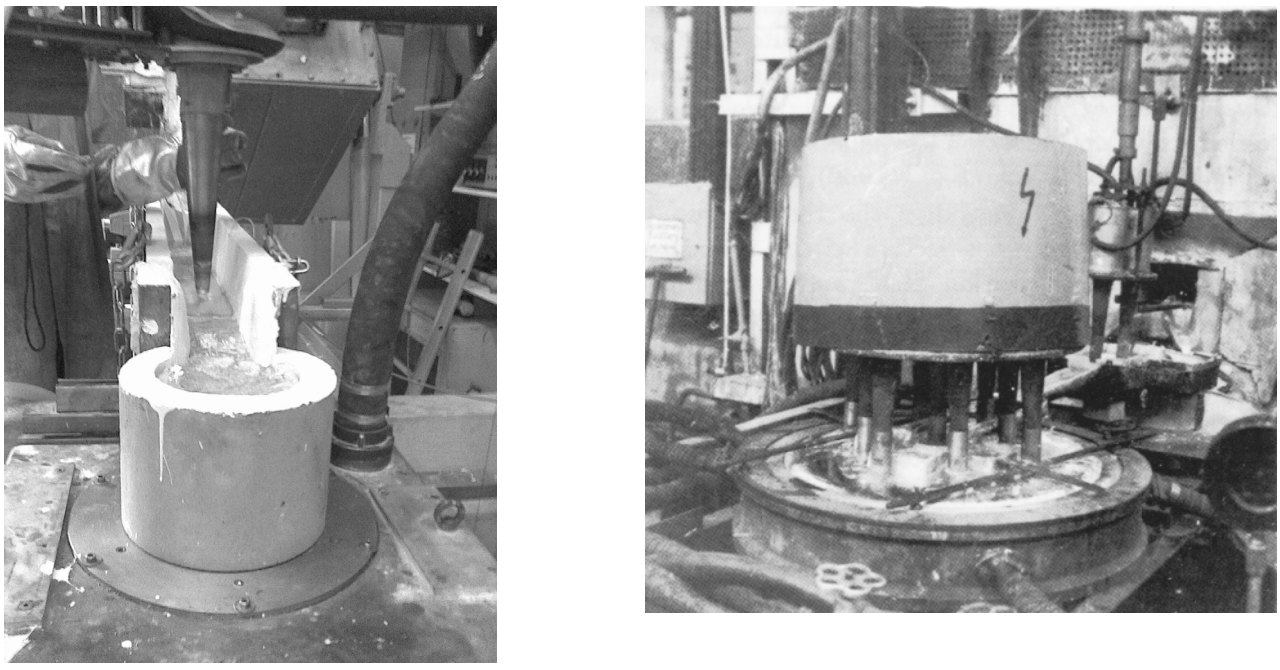
The nondendritic structure formed in billets and ingots has a positive effect on structure and properties of deformed (extruded, rolled, forged) products as has been described in detail elsewhere [9, 16]. In general hot deformed materials demonstrate more uniform and fine (sub)structure and better mechanical properties (both strength and ductility) as shown in Table 2.

Table 1. Effect of nondendritic structure on homogenization efficiency of 830-mm billets from a 7050 alloy

Homogenization time, h	El, % (tensile elongation in the temperature range of hot deformation (350–400 °C))	
	Nondendritic	Dendritic
6	75–80	60-65
16	78–80	60–65
32 (standard regime)	>80	70–75

Table 2. Mechanical properties of forged cases produced from a 7055 billet with nondendritic (numerator) and dendritic (denominator) grain structure [17]

Part of a case	Direction of sampling	UTS, MPa	YS, MPa	El, %
Bottom	Transverse Radial Height	640/590 600/570 600/540	630/570 590/550 580/530	11.8/6.8 7.2/6.8 5.3/3.2
Shell	Longitudinal Transverse	660/640 660/640	640/610 640/630	10.5/8.0 11.2/9.0



a b

Figure 9. Two practical schemes of ultrasonic melt treatment: (a) in the launder (pilot DC caster at TU Delft) and (b) in the liquid part of the sump upon casting of large round billets [9]

4. Criteria of grain refining upon cavitation melt treatment and application to commercial casting techniques

Accumulated over years experience in practical application of cavitation melt treatment to commercial alloys and casting techniques allows us to formulate some principles of successful ultrasonic melt processing [5, 8, 9]. First of all, the treated volume of melt should undergo cavitation that requires certain acoustic energy, i.e. the amplitude of ultrasonic vibrations should be above 20 μm. Secondly, the melt should contain solidification sites that can be potentially activated by cavitation, e.g. fine nonmetallic inclusions and/or intermetallic particles. In the latter case the melt processing should be performed in the temperature range of formation of such intermetallics. Thirdly, the entire melt volume should be processed by cavitation, which requires time. Hence, the optimization of the technology should be aimed at finding the best ratio between the treated volume and the availably time of treatment. Fourthly, the processing of the melt should occur as close to the solidification zone (mold) as possible with the time between the processing and the onset of solidification being preferably less than 2 min. Possible schemes of ultrasonic processing during DC casting are shown in Figure 9.

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